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Combined reflectance, electrochemical quartz crystal microbalance and conventional voltammetric measurements on high area titanium dioxide electrodes in dry, electrolyte-containing solutions of acetonitrile show that electron accumulation layer formation is coupled directly to irreversible intercalation (e.g. Li^+ or Na^+) or to quasi-reversible adsorption (tetraethylammonium ion) of charge compensating cations. Difficulty in achieving intercalation with these ions appears to account for the extreme negative shift of the flatband potential in acetonitrile, in comparison to aqueous solutions. More generally, the charge compensation based adsorption/intercalation phenomenon appears to play a key role in defining the conduction band edge energetics of titanium dioxide (and presumably other metal oxide) in solution environments.

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Energetics of Semiconductor Electrode/Solution Interfaces: EQCM Evidence for Charge-compensating Cation Adsorption and Intercalation During Accumulation Layer Formation in the Titanium Dioxide/Acetonitrile System

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Introduction

Both the relative and absolute energies of valence band and conduction band edges are important in the exploitation of semiconductors in electrochemical and photo electrochemical devices.[1] For n-type semiconductors, for example, the valence band energetics determine the photo oxidative characteristics of the semiconductor/solution interface. The absolute energy of the conduction band, on the other hand, can be a determining factor in dye sensitization of large bandgap systems. Among the more important systems requiring dye sensitization are those based on titanium dioxide – where sensitization is typically accomplished via electron injection from bipyridyl ruthenium chromophores.[2] Recent studies with these systems have emphasized nonaqueous solvents[3] and the associated interfacial energetics.[4] Among the more remarkable findings are: 1) that the flatband potential (essentially the conduction band edge) for TiO_2 in contact with nonhydroxylic solvents is shifted substantially negative of the values typically encountered with aqueous solutions, and 2) that the extent of such shifts can depend strongly on the identity of the electrolyte cation.[4]

New studies reported here offer significant insight into the chemical factors defining band edge energetics in nonaqueous solvents. The studies combine conventional electrochemical measurements with quartz crystal microbalance measurements[5] and laser reflectance measurements. They reveal that electron accumulation layer formation in nanocrystalline titanium dioxide (anatase) is crucially dependent upon charge compensating cation adsorption

(tetraethylammonium ion) or intercalation (alkali metal ions) in dry acetonitrile solutions. Conversely, the need to achieve charge compensation via one or both mechanisms appears to be a key factor in determining band edge energetics.

Experimental Section

Acetonitrile (Fisher) was distilled from calcium hydride just prior to use. Tetraethylammonium perchlorate (GFS Chemicals) was recrystallized from purified distilled water (Millipore system) and dried *in vacuo.* Lithium and sodium perchlorate were dried for several days at room temperature *in vacuo.* In some experiments, molecular sieves were also added to electrolyte solutions.

Voltammetry performed without simultaneous mass measurement was done on a PAR 273 potentiostat with a conventional three electrode arrangement. The working electrode was a gold substrate coated with a high surface area, nanocrystalline (anatase) titanium dioxide film prepared via one of two methods. The first was a slight modification of a literature method which produced films with macroscopic defects (hereafter referred to as "rough").[4] These films, while excellent for voltammetry and reflectance studies, were not sufficiently smooth for quantitative EQCM studies. To obtain films that were suitable (i.e. "smooth"), titanium dioxide colloidal suspension (24 g/L)[6] was deposited onto gold substrates by spin coating (6-7 coatings at 2000 - 2500 r.p.m.). Films were then baked at 450 ^{o}C for 1 hour in the air. All TiO_2 electrodes were stored in a desiccator until just prior to use. A platinum wire served as the counter electrode and either an s.s.c.e. or Ag wire was used as the reference electrode. (All potentials are reported vs. s.s.c.e.)

Reflectance measurements were performed with a 786 nm diode laser (Diolite). Detection was accomplished by focusing of the beam reflected from the electrode surface onto a fast photodiode (Thor Labs). Plots of photodiode voltage (reflectance) versus potential were collected on a Houston 2000 X-Y recorder.

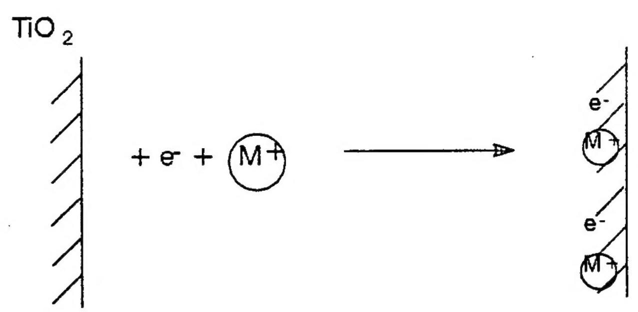
The electrochemical quartz crystal microbalance (EQCM) apparatus used was a slight modification of that employed by Ward[7] with an oscillator circuit built from the design reported by Buttry.[8] The potentiostat used was a PAR model 264A. Keyhole-shaped base electrodes (ICM) consisted of vapor deposited gold over chromium on 5 MHz, AT-cut quartz crystal substrates. The oscillator frequency was measured with a Phillips PM6681 frequency counter interfaced with a PC for data collection via a GPIB interface. Voltammograms were collected with a Houston 2000 X-Y recorder and then converted to ASCII format using the Un-Plot-It data digitizing system (Silk Scientific).

Results and Discussion

Voltammetry and electrode mass studies. In dry acetonitrile, titanium dioxide films display reductive voltammetry that can be ascribed to the formation of an electron accumulation layer. As shown in Figure 1, scanning the electrode potential in the negative direction to -1.6 V in 0.1 *M* $LiClO_4$ yields a large featureless cathodic current. Scan reversal, however, yields little or no anodic current. Interestingly, repetitive scanning results in a steady shift of the potential of current onset to more negative values, with a decrease in the amount of charge passed in each scan. Simultaneous evaluation of the relative electrode mass (via EQCM) yields irreversible

increases as evidenced by irreversible decreases in frequency of oscillation (Figure 2). Quantitative analysis of EQCM data for smooth films reveals mass increases of 7-22 grams per mole of accumulated electrons. These values are reasonably consistent with uptake of either Li^+ or Li^+ and half an equivalent of dioxygen (see below). Onset potentials for the frequency decreases correspond well with the onset potentials for current flow. In suitably dry solutions the mass increases can persist for hours or longer, even when the electrode is subsequently held at positive potentials.[9]

Related experiments (on virgin films) in 0.1 *M* $NaClO_4$/acetonitrile yielded qualitatively similar results, albeit with slightly more negative onset potentials. The calculated mass changes were 26-28 g/mole of accumulated electrons, i.e. close to the values expected either for Na^+ or Na^+ and half an equivalent of dioxygen. The striking irreversibility of the mass increases provides compelling evidence for ion uptake via an electrode charge driven intercalation mechanism rather than an adsorption mechanism:



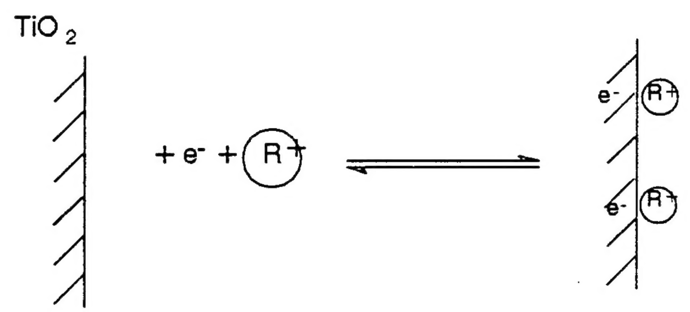
(1)

Th

e

shifts in onset potential toward more negative values in subsequent experiments can be ascribed, therefore, to the added difficulty of intercalating ions when previously intercalated ions are still present. If the accumulated electrons are captured by dissolved oxygen, then the irreversibility of the intercalation process would also appear to require O^{2-} incorporation (leading presumably to M_2TiO_3 formation).

Extension of the study to 0.05 *M* TEAP/acetonitrile yielded a much more negative onset potential (ca. -1.8 V) and a much smaller voltammetric signal. Furthermore, the signal was both largely reversible and largely unchanged by repetitive scanning. EQCM measurements also yielded small, but more-or-less reversible responses.[10] The combined findings are most easily interpreted in terms a process that is dominated by reversible adsorption initiated by accumulation layer formation:



(2)

If the driving force for adsorption is charge compensation, then the ability to adsorb only monolayer quantities (or less) of tetraethylammonium cations would place external constraints on the *extent* of electron accumulation – especially in comparison

to the intercalating systems. In any case, the apparent change in charge compensation mechanism (from intercalation to adsorption) upon replacement of Li^+ or Na^+ by TEA^+ almost certainly reflects the steric demands imposed by the tetraethylammonium ion.

Reflectance studies. Direct evidence that cation uptake and cathodic current flow are indeed associated with accumulation layer formation is provided by diode laser reflectance experiments. These experiments rely upon the near infrared absorbance of both conduction band electrons and trapped electrons in TiO_2.[4,5] As shown in Figure 3, the onset potential for reflectance attenuation (i.e., electron accumulation) in $LiClO_4$ solution is in very good agreement with the onset potentials for mass change (Figure 2) and current flow (Figure 1). Provided that air is excluded, the reflectance change – like the mass change – is irreversible. Analogous experiments in TEA^+ containing solutions yield smaller *reversible* reflectance changes at much more negative potentials, consistent with the EQCM and voltammetry findings.

Conduction band energetics. In principle, the onset potential for electron accumulation layer formation provides an approximate measure of the flatband potential and, therefore, the conduction band edge energy.[11] The experiments above clearly show that electron accumulation within TiO_2 is accompanied by ionic charge compensation at the semiconductor/solution interface (adsorption) or within the semiconductor (intercalation), rather than in solution (i.e. diffuse double layer perturbation). While it has previously been recognized that adsorption plays a role

in defining semiconductor/solution energetics, our findings and interpretation are, to the best of our knowledge, new. Thus, eqs. 1 and 2 emphasize that the *key* role of adsorption or intercalation is to balance electrostatically the excess electronic charge generated by accumulation layer formation. Effects upon flatband potentials, therefore, can be understood in much the same way as effects upon potentials in intercalation-based battery materials (e.g. manganese dioxide, vanadium oxide[12]).

Given this interpretation, the effect of cation composition upon the interfacial energetics appears to be related simply to the ease of intercalation. Electrons are most readily accumulated (i.e. flatband potentials are least negative) in acidic solutions where protons are available for charge compensation.[13] They are less easily accumulated (potentials are more negative) in Li^+ and Na^+ containing solutions, where charge compensating cation radii are larger. They are least easily accumulated (potentials are most negative) in tetraalkylammonium ion containing solutions where intercalation is sterically precluded. The values obtained for the flatband potential via this technique agree well with published data in acetonitrile[4] when identical methods of electrode preparation are used (i.e. rough electrodes). However, the smooth electrodes display much more positive onset potentials in identical electrolyte solutions. This disparity in potentials exists, however, only for the first voltammetric scan. Upon further cycling, the apparent flatband potential is nearly identical to that measured with a rough electrode. We tentatively ascribe this inconsistency to the presence of a high density of mid-gap states in the smooth electrode.[14]

The characterization of electron accumulation as a coupled cation transfer

process has interesting implications in photoelectrochemical applications. We are currently exploring these in dye-sensitized aqueous systems. Irreversible cation intercalation, on the other hand, has interesting materials synthesis implications. Most obviously, unusual new nanocrystalline metal titanates would appear to be accessible via electrochemical intercalation and subsequent oxygen incorporation.

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"Electroanalytical Chemistry", Bard, A.J. ed. Marcel Dekker Inc.: New York, NY 1991, v.17, p. 1-85.

9. Insufficiently dried solvents (or intentionally contaminated solvents) yielded reversible EQCM responses, presumably associated with proton uptake.

10. Mass changes in TEAP electrolytes do show some degree of irreversibility, suggesting behavior that is more complicated than simple adsorption/desorption.

11. For TiO_2 in $LiClO_4$ and $NaClO_4$/acetonitrile solutions the correlation is complicated by the irreversible nature of alkali metal cation intercalation. True (i.e., thermodynamic) flatband potentials, therefore, could be somewhat less negative than implied by the current, mass or reflectance onset experiments.

12. See, for example: (a) Yu, W.; Wang, D.; Zhu, B.; Zhou, G. *Solid State Comm.* **1987**, *63*, 1047. (b) Ooi, K.; Miyai, Y.; Katoh, S.; Maeda, H.; Abe, M. *Chem. Lett.* **1988**, 989.

13. Recent experiments in this lab suggest that proton intercalation accompanies accumulation layer formation in aqueous media.

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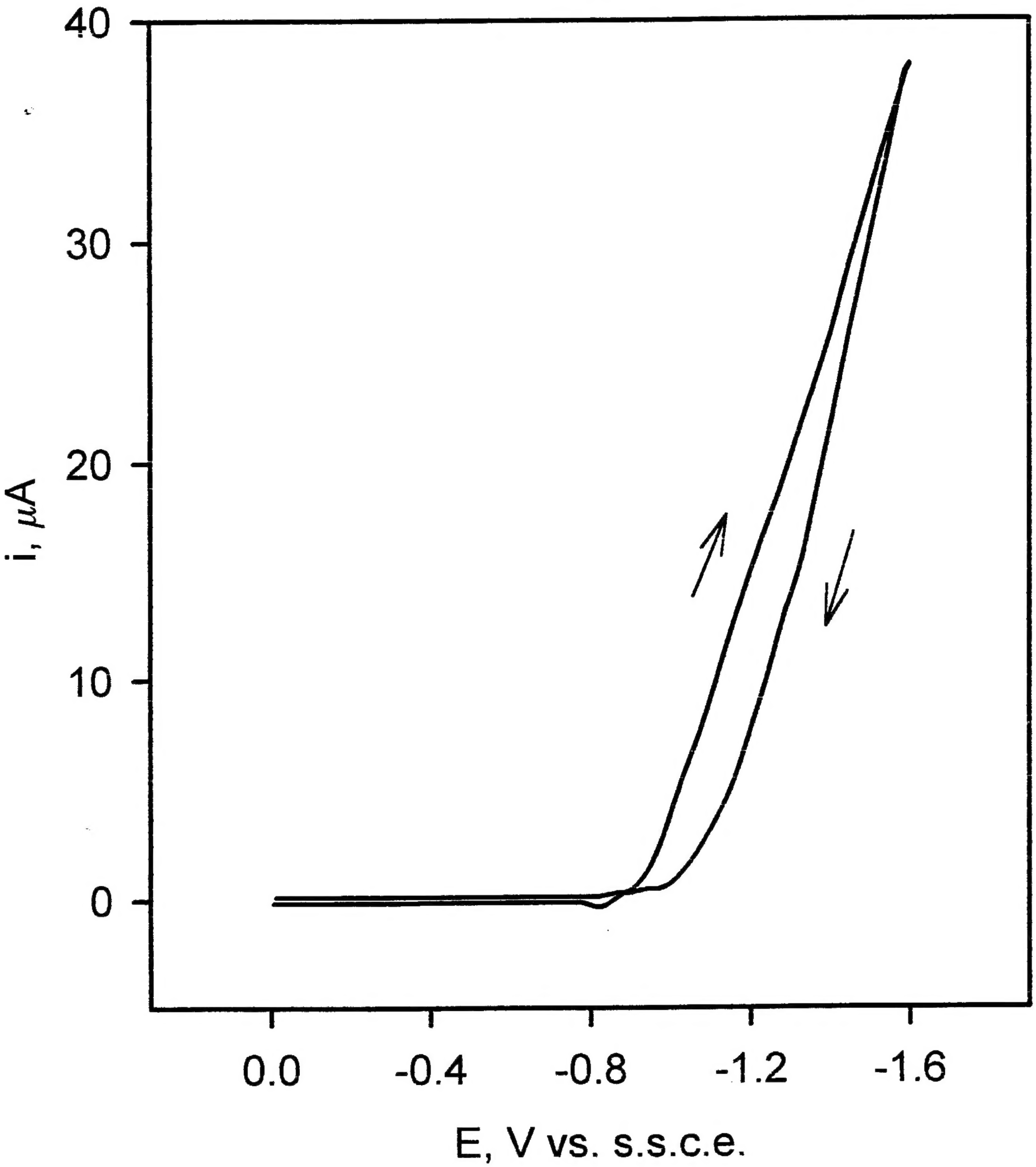
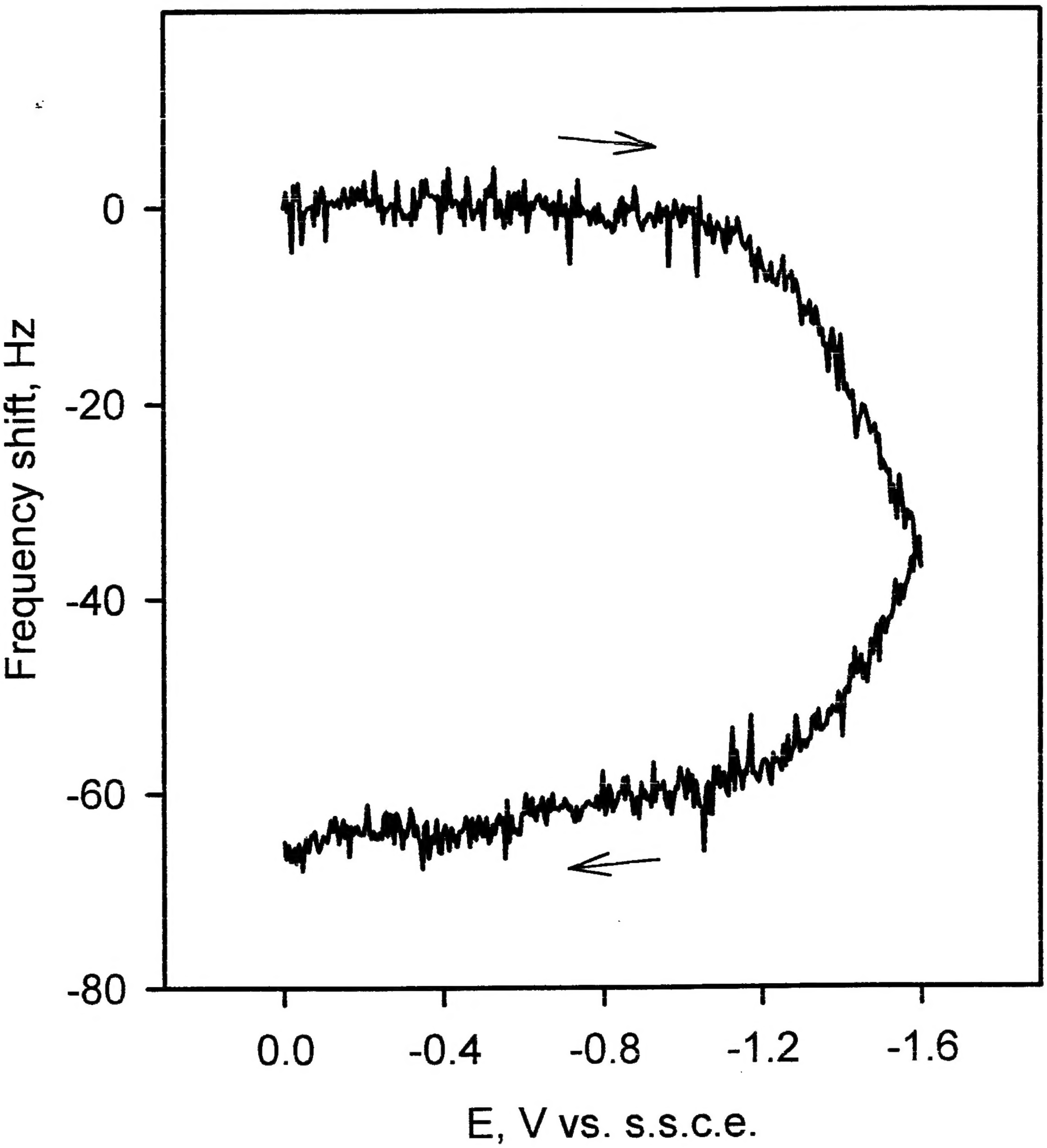
Figure Captions

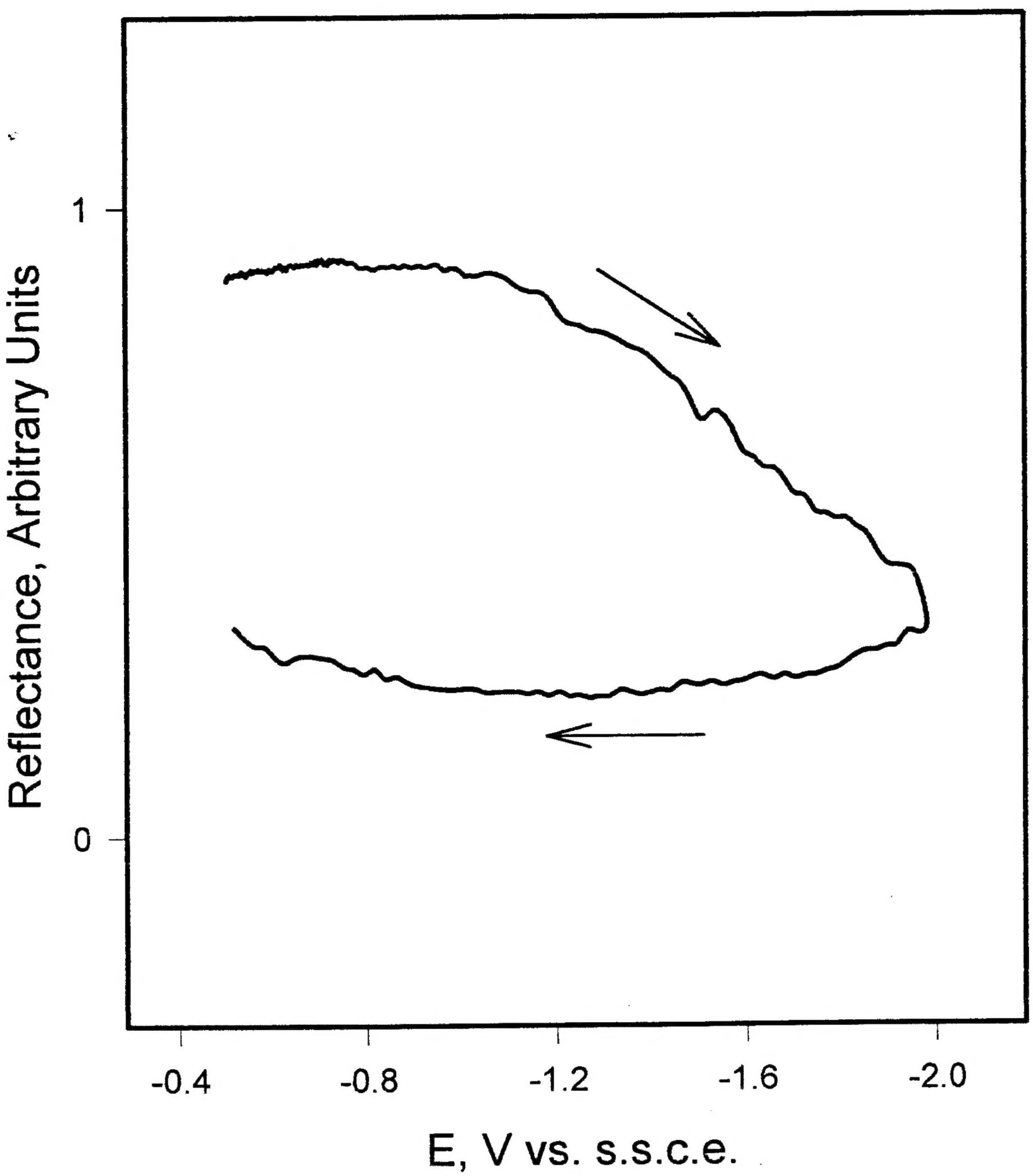
1. Voltammogram of a rough TiO_2 film on a gold electrode (second scan). Electrolyte: 0.1 *M* $LiClO_4$. Sweep rate: 50 mV/sec.

2. Frequency response of a TiO_2 coated crystal obtained simultaneously with the voltammetric scan in Figure 1.

3. Reflectance (786 nm) versus potential for a TiO_2 film. Electrolyte: 0.1 *M* $LiClO_4$. Sweep rate: 50 mV/sec.


40
30
20
10
0
i, μA
0.0
-0.4
-0.8
-1.2
-1.6
E, V vs. s.s.c.e.


0
-20
-40
-60
-80
0.0
-0.4
-0.8
-1.2
-1.6
Frequency shift, Hz
E, V vs. s.s.c.e.



Reflectance, Arbitrary Units
1
0
-0.4
-0.8
-1.2
-1.6
-2.0
E, V vs. s.s.c.e.